

**PATENT**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re patent  
appln. of: Keith C. Hong, et al.  
Appln. No: 10/600,847  
Filed: June 20, 2003  
For: **ALGAE RESISTANT ROOFING  
GRANULES WITH CONTROLLED  
ALGAECIDE LEACHING RATES,  
ALGAE RESISTANT SHINGLES, AND  
PROCESS FOR PRODUCING SAME**

Group Art  
Unit: 1762  
Examiner: Elena Tsoy  
Confirm. No. 8487  
Docket No: 008-02

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Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**APPEAL BRIEF**

Sir:

This appeal brief is being submitted electronically on December 12, 2007 in support of the Notice of Appeal filed electronically on October 12, 2007.

I. Real Party in Interest

The real party in interest is CertainTeed Corporation, a Delaware corporation.

II. Related Appeals and Interferences

There are no related appeals or interferences, other than the appeal currently pending in Application No. 10/600,809, which discloses a different process for producing algae-resistant roofing granules.

III. Status of the Claims

Claims 3, 4, 7, 11-20, 23, and 28-41 have been finally rejected.

Claims 26 and 27 were withdrawn as drawn to a non-elected invention.

The claims on appeal are claims 3, 4, 7, 11-20, 23, and 28-41.

IV. Status of Amendments

There were no amendments filed subsequent to final rejection.

V. Summary of the Claimed Subject Matter

How can you keep roofs from turning green with algae growth over a long service life?

In the roofing industry, rock is crushed to a predetermined size, 0.1 micrometer to 40 micrometer (specification, page 5, lines 27-28) for use in preparing the mineral granules that cover the asphalt shingles that cover residential roofs in many parts of our country. The granules are the structure's first line of defense against the elements. Typically, the granules are covered with a thin, highly durable colored ceramic coating, which enhances the appearance of the roof.

In some parts of this country environmental conditions favor the growth of algae on roofs. The algae growth can substantially detract from the appearance. Typically, algae growth is discouraged by incorporating a biocide into the ceramic coating on the granules (page 1, lines 19-24). The biocide slowly leaches out of the coating. However, it is difficult to control leaching from a thin coating, and the available biocide may dwindle to an ineffective level long before the anticipated life of the roof has elapsed.

The present invention addresses the problem by making use of a void-forming material to increase the porosity of an inner coating layer that incorporates biocide (page 2, line 25 - page 3, line 21).

In particular, as embodied in independent claim 3, the presently claimed invention relates to a process for producing algae-resistant roofing granules (specification, page 2, lines 32 - 33). The process includes providing inert base particles and forming first intermediate particles by coating the inert base particles with a first mixture to form a first layer (page 3, lines 1 - 3). The first mixture includes at least one algaecidal material and a void-forming material (page 3, lines 4-5). The algaecidal material comprises cuprous oxide (page 3, lines 24-25). The void-forming material releases gaseous material at temperatures above 90 degrees C and has an average particle size no larger than 2 mm (page 3, lines 7 - 9). The process further includes forming second intermediate particles by coating the first intermediate particles with a second mixture that includes a binder and a coloring material but does not include a void-forming material (page 3, lines 12-17). The process also includes heating the second intermediate particles to release the gaseous material to form pores in the first layer to produce the roofing granules (page 3, lines 18-21). The roofing granules produced by this process inherently have a dark brown color. When the second intermediate particles are heated to cure the coating material, the roofing granules turn dark brown in color from the cuprous oxide (Evidence Appendix, Exhibit A, Declaration Under Rule 132 of Dr. Keith C. Hong, paragraph 4).

As embodied in independent claim 28, the presently claimed invention also relates to a process for producing algae-resistant roofing granules (page 2, lines 32-33). The process includes providing inert base particles and forming first intermediate particles by coating the inert base particles with a first mixture to form a first layer (page 3, lines 1 - 3). The first mixture includes a binder, at least one algaecidal material, and a void-forming material (page 3, lines 4-5). The void-forming material releases gaseous material at temperatures above 90 degrees C and has an average particle size no larger than 2 mm (page 3, lines 7 - 9). The process further includes forming second

intermediate particles by coating the first intermediate particles with a second mixture that includes a binder and a coloring material but does not include a void-forming material (page 3, lines 12-17). The second coating has a thickness of from about 3 micrometers to 25 micrometers (page 8, lines 21-22). The process also includes heating the second intermediate particles to release the gaseous material to form pores in the first layer to produce the roofing granules (page 3, lines 18-21). The relatively thick, pigmented outer layer would inherently mask or hide the inner layer (Evidence Appendix, Exhibit A, Declaration Under Rule 132 of Dr. Keith C. Hong, paragraph 7).

VI. Grounds of Rejection To Be Reviewed On Appeal

A. Claims 3, 4, 7, 11, 16-21, 23, 28-32 and 36-41 were finally rejected as being unpatentable under 35 U.S.C. § 103(a) over U.S. Patent 3,528,842 ("Skadulis") in view of U.S. Patent 4,378,408 ("Joedicke").

B. Claims 3, 4, 7, 11, 16-21, 23, 28-32 and 36-41 were finally rejected as unpatentable under 35 U.S.C. § 103(a) as being unpatentable over Skadulis in view of U.S. Patent 3,918,407 ("Greenberg").

C. Claims 12-13 and 33 were finally rejected as being unpatentable under 35 U.S.C. § 103(a) over Skadulis in view of Joedicke, or Skadulis in view of Greenberg, and further in view of U.S. Patent 3,507,676 ("McMahon").

D. Claims 14-15 and 34-35 were finally rejected as being unpatentable under 35 U.S.C. § 103(a) over Skadulis in view of Joedicke, or Skadulis in view of Greenberg, and further in view of U.S. Patent 4,430,108 ("Hojaji et al.").

VII. Argument

A. The Examiner's Reading of Joedicke and Skadulis Is Incorrect

A key issue in this appeal is the correct reading of Joedicke and Skadulis.

The Examiner reads a single sentence in Joedicke literally; but fails to read Joedicke as a whole for what it would impart to one of ordinary skill in the art. Applicants contend that the correct reading is that which a person of ordinary skill would understand from Joedicke, taken as a whole. Simply put, Joedicke introduces microvoids into the coating layers covering roofing granules for the purpose of scattering light, so as to be able to reduce the amount of expensive white titanium dioxide pigment otherwise required. Applicants contend that one of ordinary skill in the art would understand that it would be useless to introduce microvoids into invisible inner layers, since such layers could not scatter incident light.

Applicants' reading of Joedicke is supported by the evidence of record, namely, the declaration of Dr. Keith Hong (Evidence Appendix, Exhibit A, Declaration Under Rule 132, paragraph 7).

The Examiner focuses on a single sentence in Joedicke that states that "Granules may be coated in one or more coats with any desired amount of coating material and gas forming compound may be used in any one or more of the coatings." (col. 5, lines 38-42). The Examiner reads this to mean that, "according to Joedicke, lightening of roofing granules can be achieved by inclusion of a gas-forming compound into any layer of a multiple layers. Therefore, one of ordinary skill in the art would have reasonable expectation of success in achieving lightened roofing granules by including of a gas-forming compound *either* into a first layer *or* outer layer with no preferences" (sic, Examiner's Action dated July 24, 2007, page 4, second paragraph, emphasis in original).

The Examiner's position is contradicted by of the common sense understanding of one of ordinary skill in the art of the disclosure of Joedicke as a whole.

The Examiner takes a similar incorrect view of Skadulis. The Examiner notes that Skadulis teaches that titanium dioxide may be added to the coating composition to impart the desired color to the coating (Examiner's Action date July 24, 2007, page 4, last paragraph, referencing col. 3, lines 29-32). From this disclosure, the Examiner takes the position, contrary to common sense, that "[s]ince Skadulis does not say to which layer the pigment should be added, it should be assumed that TiO<sub>2</sub> may be added to any layer" (Id., emphasis in original).

The Examiner's readings of Joedicke and Skadulis are similar to the PTO's reading of the Macaulay reference in In re Wright, 866 F.2d 422, 9 USPQ2d 1649 (Fed. Cir. 1989). In that case applicant's claims included the step of depositing a layer of photosensitive microcapsules in the form of a free-flowing powder. The PTO rejected the claims as obvious over Macaulay, which stated that Macaulay's invention "does not require an aqueous coating system." The Federal Circuit reversed, stating that the PTO's attempt to show that Macaulay suggested the applicant's invention consisted of taking statements wholly out of context and giving them meanings they would not have had to one skilled in the art having no knowledge of applicant's invention, or to anyone else who can read the specification with understanding." 866 F.2d at 426, 9 USPQ2d at 1652. A single line in a reference should not be taken out of context and relied upon with the benefit of hindsight to show obviousness. A reference should be considered as a whole. Bausch & Lomb, Inc. v. Barnes-Hind/Hydrocurve, Inc. 796 F.2d 443, 230 USPQ 416 (Fed. Cir. 1987). It is not permissible to pick and choose from any one reference only so much as will support a given position, and ignore other parts necessary to a full appreciation of what the reference fairly suggests to one of ordinary skill in the art. In re Wesslau, 353 F.2d 238, 241, 147 USPQ 391, 393 (CCPA 1965).

One of ordinary skill in the art, or indeed anyone who has ever redecorated a room with a paintbrush, would understand that Joedicke's statement that microvoids

could be created for the purposes of lightening any *visible* layer. Thus, if a coating were formed from several layers, with the outermost layers not completely opaque, microvoids could be advantageously formed in an inner layer visible through the partially transparent outer layers, where the microvoids could effectively serve Joedicke's light scattering purpose. The Examiner admitted as much when she construed Skadulis to disclose a transparent outer layer (Examiner's Action dated March 7, 2007, page 7, subsection (B)). When redecorating a room, two or more coats of the new paint may be required to hide the old paint, because each of the new coating layers is partially transparent and the old paint may show through unless the cumulative coating is thick enough to scatter enough incident light so that no significant amount is reflected back from the old paint.

Joedicke discloses a preferred embodiment which is "in accordance with conventional practice," and which, while forming two layers of coating composition on the base granule, employs neither gas forming compounds nor titanium dioxide in the inner layer (col. 5, lines 44-62). Each of the two layers is preferably between 0.01 mm and 0.02 mm thick. One of ordinary skill in the art the outer layer of this preferred embodiment would hide the inner layer from view, so that forming microvoids or adding the light-scattering pigment titanium dioxide would be a futile expense. Similarly, Joedicke '408's only actual examples of the practice of his invention, Trials Nos. 1 and 2 of Example 2, two-coat granules are employed, with the initial coat containing no microvoids (col. 6, line 51 - col. 7, line 38). Joedicke's examples and preferred embodiment are consistent with the common sense understanding of one of ordinary skill in the art that there would be no point in forming microvoids in inner layers that were not visible through outer layers. Similarly, Skadulis does not say that the titanium dioxide should be included in the visible exterior layer or layers because it can be included in any layer, including invisible interior layers, as contended by the Examiner,

because one of ordinary skill in the art can be assumed to have a modicum of common sense, and would understand that it would be ineffective and wasteful to include this expensive pigment in an invisible inner layer.

The Examiner's literal reading of the single sentence in Joedicke, and of Skadulis, is wrong because it is inconsistent with the common sense understanding of one of ordinary skill in the art of Joedicke and Skadulis as a whole.

B. The Cited Combination of References Do Not Make Out  
a *Prima Facie* Case of Obviousness with Respect to  
Claims 3, 4, 7, 11, 16-21, 23, 28-32 and 36-41

In making her rejection, the Examiner stated that the outer layer of Skadulis carrying no algaecide may be formed as a very thin layer so that it would not cover the color of the first layer (Examiner's Action dated March 6, 2007, page 2, Paragraph 2). This is simply speculation on the part of the Examiner. There is nothing in the reference cited which supports the Examiner's speculation. The Examiner's speculation is contrary to the common sense expectation of one of ordinary skill in the art.

Skadulis does not even discuss forming multiple coating layers, but merely includes three working examples in which two layers were formed. In Example I a first coating composition including rutile titanium dioxide is applied to the base granule and fired to 950 degrees F. After cooling a second coating composition is "applied to the colored pre-coated granules in the mixer, following which the granules were fired to 700 ° F. to insolubilize the silicate coating (col. 4, lines 43 - 46). The second coating composition includes both rutile titanium dioxide and cuprous oxide, so that "[t]he resulting granules had a very slightly reddish off-white color" (col. 4, lines 47-48). In Example II cuprous bromide was substituted for the cuprous oxide of Example I, but there is no disclosure regarding the color of the granules. In Example II, titanium dioxide was omitted from the first coating composition, and cobalt blue stain was added to the

second coating composition, so that “[t]he resulting granules were bluish-gray in color . . . .” (col. 5, line 32).

There is nothing in Skadulis to suggest it would even be possible to form a transparent outer layer as the Examiner speculates.

In each of the three examples, Skadulis discloses adding titanium dioxide to the outer layer to color the layer. There is nothing in Skadulis to suggest that the titanium dioxide should or could be omitted. In addition, in both layers and in each example, the coating binder is sodium silicate with kaolin clay dispersed therein.

Because Skadulis requires a coating sufficiently porous to permit leaching of metal ions from the granule coating, Skadulis employs as a binder sodium silicate and clay which is fired to a temperature above the dehydration point of the sodium silicate but below the melting point of the clay (col. 3, lines 16 - 32). A discussion of physical changes that occur during the drying and firing of clay is provided in Chapter 4 of D. Rhodes, Clay and Glazes for the Potter (Chilton Book Company, Radnor, PA, 1973, Evidence Appendix, Exhibit B). Skadulis expressly rejects using prior art methods, such as disclosed in U.S. Patent 1,782,649, which provide impermeable glazes (col. 3, lines 54-60). Because Skadulis fires his coatings to temperatures below the melting point of the clay, one of ordinary skill in the art would expect that the clay in the insoluble coatings to be in the form of a light-scattering, crystalline particulate. Contrary to the Examiner’s speculation, one of ordinary skill in the art would have no reason to expect that such a coating would become transparent no matter how thinly it is applied. Further, there is nothing in Skadulis which would suggest to one of ordinary skill in the art that the coating composition should be thinly applied. On the contrary, in his examples, Skadulis applies a coating at least thickly enough to result in “colored granules” in every case.

Even if the Examiner's speculation were technically accurate and legally proper, it would not be applicable to applicants' claims 28-41, which require that the second coating have a thickness of from about 2 micrometers to 25 micrometers (independent claim 28).

With respect applicants' argument that one of ordinary skill in the art would not be provided any suggestion or incentive by Joedicke to add gas-forming material to an interior coating layer for a roofing granule where the exterior layer itself contained a significant amount of light-scattering pigment, such as titanium dioxide, the Examiner incorrectly characterized Skadulis as teaching that the appropriate pigments generally metal oxides such as titanium dioxide may be added to any layer (referencing Examples I-III; and column 3, lines 29-32), and also incorrectly stated that they may be added, for example, only to the first layer (referencing Example I) to impart the desired color to the coatings (referencing column 3, lines 29-32).

Skadulis discloses the use of titanium oxide in the inner layer of two of his three examples (I and II), but omits titanium oxide completely from his third example. Nowhere does he say that appropriate pigments may be added to any layer. There is no example of adding titanium oxide only to the first layer, contrary to the Examiner's statement. In Examples I and II titanium dioxide is added to both layers. The "take home" lesson for one of ordinary skill in the art from Skadulis' set of example is that it is not necessary to add any coloring pigment to the inner layer - the third example omits titanium dioxide from the inner layer and yet provides a suitable colored resulting granule. So, why add expensive pigment to the inner layer where it will not be visible? The Examiner's contrary understanding of the significance is not correct.

Regarding applicants' argument that one of ordinary skill in the art would find Joedicke largely irrelevant to the preparation of dark-colored roofing granules, because whereas light- or white-colored roofing granule coatings include materials such as

titanium dioxide that reflect light, dark colored roofing granule coatings include material that absorb rather than reflect light, and thus have a dark color, the Examiner misconstrues the significance of the cited references. The Examiner found this argument unconvincing because Skadulis teaches roofing granule coatings having (any) desired color by addition of metal oxide pigments including titanium dioxide (e.g. light grey color), and that consequently one of ordinary skill in the art would find Joedicke '408 largely relevant to the preparation of light colored roofing granule coatings of Skadulis. Even if this were correct, it is not relevant to applicants' dark colored granules (Claims 3, 4, 7, 11-20, and 23) containing copper. The properly framed issue is not whether Joedicke is relevant to Skadulis, but whether Skadulis and Joedicke are relevant to the presently claimed invention.

The evidence of record is that one of ordinary skill in the art would understand that the formation of microvoids, such as disclosed by Joedicke, for the purpose of lightening the coating of roofing granules, would be detrimental to the appearance of dark colored, copper containing granules, such as those produced by the process claimed in Claims 3, 4, 11-20 and 23 (Evidence Appendix, Exhibit A, Declaration Under Rule 132, paragraph 8). Consequently, Joedicke does not suggest the formation of microvoids in such copper containing roofing granule coatings.

The combination of Skadulis and Joedicke fails to make out a *prima facie* case of obviousness. The rejection over Skadulis in view of Joedicke should be reversed for these reasons.

D. The Cited Combination of References Is Improper and Cannot Render Claims 3, 4, 7, 11, 16-21, 23, 28-32 and 36-41 Obvious

1. The Secondary Reference Greenberg Is Non-analogous Art

In making her final rejection, the Examiner reconstructs applicants' invention by agglomerating references from two different, unrelated arts. Since the secondary

reference the Examiner relies upon is neither in the same field of endeavor (producing roofing granules) nor reasonably pertinent to the problem of providing long term algae resistance, her rejection is not based on the relevant prior art, and she has not made a *prima facie* case of obviousness. The Board should reverse her rejection for this reason.

Skadulis relates to manufacture of roofing granules. Greenberg relates to the art of controlling fleas on warm blooded animals, such as dogs and cats, by application of an insecticidal gas generation device. Applicants respectfully submit that one of ordinary skill in the roofing granule art would not look to the flea control art to solve the problem of long term algae resistance.

A prerequisite to determining whether a claimed invention would have been obvious to one of ordinary skill in the art in view of the art cited by the Examiner is determining what is "prior art, an issue frequently couched in terms of whether the cited art is "analogous" or too remote to be treated as prior art. In re Clay, 966 F.2d 656, 657, 23 USPQ2d 1058 (Fed. Cir. 1992), citing In re Sovish, 759 F.2d 738, 741, 226 USPQ 771, 773 (Fed. Cir. 1985).

Two criteria can be applied to determine whether cited art is analogous. The first criterion is whether the cited art is from the same field of endeavor, regardless of the problem being addressed by the inventor. The second criterion is whether the reference is still reasonably pertinent to the particular problem being solved by the inventor, assuming the reference is not in the same field of endeavor. In re Clay, 966 F.2d 656, 658-59 (Fed. Cir. 1992), citing In re Deminski, 796 F.2d 436, 442, 230 USPQ 313, 315 (Fed. Cir. 1986); In re Wood, 599 F.2d 1032, 1036, 202 USPQ 171, 174 (CCPA 1979).

## 2. Greenberg Relates to a Different Field of Endeavor

The present invention and Skadulis each relate to the same general field of endeavor - protective granules for roofing.

As stated in the “field of the invention” section of the application on appeal, “[t]he present invention relates to asphalt roofing shingles, protective granules for such shingles, and process for making such granules and shingles” (page 1, line 10-11).

In the same vein, Skadulis et al. states that “[t]his invention relates to inorganic coatings for outdoor surfacing having algicidal and/or fungicidal properties, to articles such as roofing granules coated therewith, and to methods for protecting surfaces from the growth of algae thereon” (col. 1, lines 24-28).

In contrast, Greenberg relates to a wholly different field.

Greenberg, in the field of invention section, states that “[t]his invention relates to the control of fleas on warm blooded animals, such as dogs and cats, by application of an insecticidal gas generator device. More particularly, this invention relates to novel compositions and to methods of manufacture of a pet collar comprised of a synthetic resin such as polyvinyl chloride (PVC) having dispersed therein the insecticide dimethyl 1,2-dibromo-2,2-dichloroethyl phosphate, commonly known as naled.” (col. 1, lines 4-12).

One of ordinary skill in the art seeking to make algae resistant roofing granules would not look to the pesticidal pet collar art for guidance.

The Examiner does not attempt to dispute that Greenberg relates to a different field of endeavor.

3. Greenberg Is Not Reasonably Pertinent to the Problem Solved by the Present Invention

The Examiner contends that Greenberg is reasonably pertinent to the particular problem with which applicants were concerned. However, this is not correct.

The particular problem of the present invention at hand involves algae growth on roofs by release of sparingly soluble metal ions. Greenberg does not attempt to resolve any such problem, but rather the problem of continuous release of a volatile gaseous

insecticide having a low vapor pressure from plastic flea collars. Because Greenberg substituted "naled," that is, dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate for the DDVP, dimethyl 2,2-dichlorodivinyl phosphate, more conventionally used, and because naled has a lower vapor pressure than DDVP, the rate of release of naled from polyvinylchloride collars was less than the optimum dosage to protect the pet wearing the collar from fleas. Greenberg simply increased the surface area of the collar by adding a "porosity control agent" to make the flea collar surface porous. The present invention addresses an entirely different problem. The initial rate of release of algacidal metal ions is not the problem - but rather obtaining a more effective and efficient use of the algacide so that release can be tailored to specific anticipated environmental situations. Greenberg is simply not at all pertinent to this problem.

The Examiner attempts to bootstrap her position by asserting that the "art of a controlled release of an active substance does not differentiate what is being released from a porous carrier" reciting a wash list of "active substances" recited in U.S. Patent 5,876,752 ("Herbig et al.") (Examiner's Action dated July 24, 2007, page 6, first paragraph). The Examiner reasoning here is not correct. Herbig et al. discloses a very special kind of "porous carrier," namely "a tablet, capsule or bead for administration to a mammal which releases one or more pharmaceutically active substances into said animal over an appreciable time interval which comprises a core of said active substance or substances, with or without one or more pharmaceutically acceptable excipients, said core being surrounded by a porous substructure and one or more IF (i.e. "interfacially polymerized") membranes" (col. 2, lines 24 - 31). Now while it may be that controlled release capsules including "a porous substructure" and "one or more interfacially polymerized membranes" are indifferent as to what is being released, as the Examiner appears to conclude from the wash list. However, there is no logical reason to believe that this peculiar property of these special controlled release structures is

generally true of the rest of the extensive “art of controlled release of an active substance.” In addition, the Examiner’s characterization is likely wrong even if limited to Herbig et al. One of ordinary skill in the art would understand from Herbig et al. that the active substances in the wash list are not like variously colored marbles falling through a sieve. One of ordinary skill in the art would expect the possibility of unique chemical and physical interactions between the release structure and the active substance, based on fundamental chemical principles. The “principle” the Examiner relies upon contradicts common sense. Herbig et al. is currently classified in class 424, subclass 473, the triple dot-indented subclass being defined as “drug, bio-affecting and body treating compositions, preparations characterized by; special physical form; tablets, lozenges, or pills; sustained or differential release type; layered unitary dosage forms; with porous, perforated, apertured, or sieved layer (e.g., dialyzing layer, microporous layer, etc.).” This is far removed from roofing granules, and one of ordinary skill in the art of preparing roofing granules would have little expectation of finding anything relevant to his or her problems in such art.

The Examiner’s citation of Greenberg contradicts the Federal Circuit’s admonition to the PTO “that it is necessary to consider the ‘reality of the circumstances’ - in other words, common sense - in deciding which fields a person of ordinary skill would reasonably be expected to look for a solution to the problem facing the inventor.” In re Bigio, 381 F.3d 1320, 1326, 72 USPQ2d 1209 (Fed. Cir. 2004), citing In re Oetiker, 977 F.2d 1443, 1447, 24 USPQ2d 1443 (Fed. Cir. 1992). In the Oetiker case, the applicant claimed an improvement in a hose clamp which differed from the prior art in the presence of a pre-assembly “hook” which maintained the pre-assembly condition of the clamp and disengaged automatically when the clamp was tightened. The Board had relied upon a reference which disclosed a hook and eye fastener for use in garments, reasoning that all hooking problems are analogous. The Federal Circuit held the

reference was not within the field of applicant's endeavor, and was not reasonably pertinent to the particular problem with which the inventor was concerned because it had not been shown that a person of ordinary skill, seeking to solve a problem of fastening a hose clamp, would reasonably be expected or motivated to look to fasteners for garments. Here there is no showing why one of ordinary skill in the roofing granule art would look to the pet collar art for guidance.

Similarly, Greenberg is presently classified in U.S. class 119, "animal husbandry." The present application has been classified in U.S. class 52, "static structures (e.g., buildings)." These arts are wholly unrelated. The Examiner argues that it is well settled that references do not have to be classified by the PTO in the same class to be pertinent, citing In re Mlot-Fijalkowski, 213 USPQ 713 (CCPA 1982) (Examiner's Action dated July 24, 2007, page 9, first paragraph). However, applicants merely contend that the difference in classification is some evidence that Greenberg is not pertinent to the problem addressed by applicants.

Greenberg is not analogous prior art. This rejection should be reversed for this reason.

E.     The Cited Combination of References Do Not Make  
Out a *Prima Facie* Case of Obviousness with Respect  
to Claims 3, 4, 7, 11, 16-21, 23, 28-32 and 36-41

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As in the case of the first rejection entered under Section 103(a), even if all the art relied upon by the Examiner were actually analogous art, the combination proposed by the Examiner fails to make a *prima facie* case of obviousness.

Even if Greenberg were part of the content of the relevant prior art, the Examiner's suggested combination with the Skadulis would not render the presently claims obvious. Greenberg solves his (unrelated) problem by increasing the surface porosity of the flea collars (col. 5, lines 17-28): "The main function of the additive is to provide a surface porosity which preferably includes pores extending part way down into

the body of the collar.” This is achieved by employing an additive which has a boiling point at or below the curing temperature of the polyvinylchloride resin. Adding some low boiling additive to increase the surface porosity of roofing granules would not provide the presently claimed invention - the porosity of the outer layer that forms the surface would be increased - not that of the inner layer. Thus, the combination of Skadulis and Greenberg does not even meet the limitations of applicants’ presently claimed invention, but rather teaches one of ordinary skill in the art away from that invention. The combination of Skadulis and Greenberg fails to establish a *prima facie* case of obviousness.

The Examiner has failed to make out a *prima facie* case of obviousness with respect to Claims 3, 4, 7, 11, 16-21, 23, 28-32 and 36-41, and this rejection should be reversed for this reason.

F. The Cited Combination of References Do Not Make Out a *Prima Facie* Case of Obviousness with Respect to Claims 12, 13 and 33

Claims 12 , 13 and 33 stand finally rejected under 35 U.S.C. 103(a) as being unpatentable over Skadulis in view of Joedicke, or Skadulis in view of Greenberg, and further in view U.S. 3,507,676 (“McMahon”). As in the case of the first and second rejections entered under Section 103(a), even if all the art relied upon by the Examiner were actually analogous art, the combination proposed by the Examiner still fails to make a *prima facie* case of obviousness.

Even were the references combined as suggested by the Examiner, there would be nothing to teach or suggest to one of ordinary skill in the art to include void-forming material in the inner coating layer but not in the outer coating layer of roofing granules containing cuprous oxide, or to the inner coating layer of roofing granules have an opaque outer layer. McMahon does not add anything to the combination of Skadulis in view of Joedicke in this regard, or to Skadulis in view of Greenberg.

The Examiner contends that Skadulis broadly teaches that titanium dioxide may be added to any layer, and that Joedicke '408 teaches that lightening of roofing granules can be achieved by inclusion of a gas forming compound into any layer of a roofing granule coating having multiple layers (Examiner's Action dated July 24, 2007, page 8, third paragraph). This is not correct. One of ordinary skill in the art, applying common sense to Joedicke's and Skadulis' disclosures, would understand that a roofing granule coating could not be lightened by adding titanium dioxide pigment to, or by forming microvoids in, invisible inner coating layers.

The cited combination of references thus does not establish a *prima facie* case of obviousness in respect of the presently claimed invention, as claimed by Claims 12, 13 and 33. There is nothing that discloses or would suggest the presently claimed process to one of ordinary skill in the art. The Examiner's rejection of claims 12, 13 and 33 should be reversed by the Board for this reason.

G. The Cited Combination of References Do Not Make Out a *Prima Facie* Case of Obviousness with Respect to Claims 14-15 and 34-35

Claims 14-15 and 34-35 stand finally rejected under 35 U.S.C. 103(a) as being unpatentable over Skadulis in view of Joedicke, or Skadulis in view of Greenberg, and further in view of U.S. Patent 4,430,108 ("Hojaji"). As in the case of the first, second, and third rejections entered under Section 103(a), even if all the art relied upon by the Examiner were actually analogous art, the combination proposed by the Examiner still fails to make a *prima facie* case of obviousness.

Applicants contend that Hojaji does not supply the teaching or suggestion missing from the combination of Skadulis and Joedicke, or of Skadulis and Greenberg, that void-forming material be included in the inner layer composition but excluded from the outer layer composition in either a composition including cuprous oxide or a roofing granule with an opaque outer layer. Consequently, the cited combination of prior art

references does not make a *prima facie* case of obviousness of the claims as presently amended.

The cited combination of references thus does not establish a *prima facie* case of obviousness in respect of the presently claimed invention, as claimed by Claims 14 and 15. There is nothing that discloses or would suggest the presently claimed process to one of ordinary skill in the art. The Examiner's rejection of claims 14 and 15 should be reversed by the Board for this reason.

VIII. Conclusion

Each of Examiner's rejections under 35 U.S.C. 103(a) should be reversed by the Board. Even were the Examiner's reasoning correct, each rejection is based on a misunderstanding of the disclosure of Joedicke, and consequently cannot make a *prima facie* case of obviousness. Further, three of the four rejections are based on nonanalogous art which should not be considered in testing the nonobviousness of the presently claimed invention under Section 103(a).

Respectfully submitted,

December 12, 2007

/Alex R. Sluzas/  
Alex R. Sluzas, Esq.  
Reg. No. 28,669

Order No. 5672

PAUL AND PAUL  
Suite 2900  
Two Thousand Market Street  
Philadelphia, PA 19103  
215-568-4900

# CLAIMS APPENDIX

## CLAIMS ON APPEAL:

Claim 3. A process for producing algae-resistant roofing granules, the process comprising:

- (a) providing inert base particles;
- (b) forming first intermediate particles by coating the inert base particles with a first mixture including;
  - at least one algaecidal material comprising cuprous oxide, and
  - a void-forming material, the void-forming material releasing gaseous material at temperatures above 90 °C, and having an average particle size no larger than 2 mm,to form a first layer on the inert base particles;
- (c) forming second intermediate particles by coating the first intermediate particles with a second mixture including a binder and a coloring material and not including a void-forming material; and
- (d) heating the second intermediate particles to release the gaseous material and form pores in the first layer to produce the roofing granules.

Claim 4. A process according to claim 3 wherein the first mixture further includes a binder, the binder comprising an aluminosilicate material and an alkali metal silicate.

Claim 7. A process according to claim 3 wherein the second mixture further includes a binder, the binder comprising an aluminosilicate material and an alkali metal silicate.

Claim 11. A process according to claim 3 wherein the cuprous oxide comprises at least 2 percent of the algae resistant granules.

- Claim 12. A process according to claim 3 wherein the at least one algaecidal material further comprises zinc oxide.
- Claim 13. A process according to claim 12 wherein the zinc oxide comprise at least 0.1 percent by weight of the algae-resistant granules.
- Claim 14. A process according to claim 3 wherein the void-forming material comprises a substance selected from the group comprising ground walnut shells, sugar, and carbon black.
- Claim 15. A process according to claim 14 wherein the void-forming material comprises at least 0.1 percent by weight of the algae-resistant granules.
- Claim 16. A process according to claim 3 wherein the coloring material is selected from the group comprising transition metal oxides.
- Claim 17. A process according to claim 3 wherein the second intermediate particles are heated to a temperature of at least 500 degrees C.
- Claim 18. A process according to claim 3 wherein the granules have a pore size in the range of about 0.1 to 20  $\mu\text{m}$ .
- Claim 19. A process according to claim 3 wherein the first intermediate layer has a thickness of about 30  $\mu\text{m}$ .
- Claim 20. A process according to claim 3 wherein the second intermediate layer has a thickness of about 5  $\mu\text{m}$ .
- Claim 23. A process according to claim 21 wherein the second mixture further includes at least one algaecidal material.
- Claim 28. A process for producing algae-resistant roofing granules, the process comprising:
- (a) providing inert base particles;

- (b) forming first intermediate particles by coating the inert base particles with a first mixture including;
  - a binder;
  - at least one algaecidal material, and
  - a void-forming material, the void-forming material releasing gaseous material at temperatures above 90 °C, and having an average particle size no larger than 2 mm,to form a first layer on the inert base particles;
- (c) forming second intermediate particles by coating the first intermediate particles with a second mixture including a binder and a coloring material and not including a void-forming material to form a second coating having a thickness of from about 2 micrometers to about 25 micrometers; and
- (d) heating the second intermediate particles to release the gaseous material and form pores in the first layer to produce the roofing granules.

Claim 29. A process according to claim 28 wherein the first mixture includes a binder comprising an aluminosilicate material and an alkali metal silicate.

Claim 30. A process according to claim 28 wherein the second mixture includes a binder comprising an aluminosilicate material and an alkali metal silicate.

Claim 31. A process according to claim 28 wherein the at least one algaecidal material is selected from the group consisting of copper compounds and zinc compounds.

Claim 32. A process according to claim 28 wherein the at least one algaecidal material is cuprous oxide; the cuprous oxide comprising at least 2 percent of the algae resistant granules.

Claim 33. A process according to claim 32 wherein the at least one algaecidal material further comprises zinc oxide, the zinc oxide comprising at least 0.1 percent by weight of the algae-resistant granules.

Claim 34. A process according to claim 28 wherein the void-forming material comprises a substance selected from the group comprising ground walnut shells, sugar, and carbon black.

Claim 35. A process according to claim 28 wherein the void-forming material comprises at least 0.1 percent by weight of the algae-resistant granules.

Claim 36. A process according to claim 28 wherein the coloring material is selected from the group comprising transition metal oxides.

Claim 37. A process according to claim 28 wherein the second intermediate particles are heated to a temperature of at least 500 degrees C.

Claim 38. A process according to claim 28 wherein the granules have a pore size in the range of about 0.1 to 20  $\mu\text{m}$ .

Claim 39. A process according to claim 28 wherein the first intermediate layer has a thickness of about 30  $\mu\text{m}$ .

Claim 40. A process according to claim 28 wherein the second intermediate layer has a thickness of about 5  $\mu\text{m}$ .

Claim 41. A process according to claim 28 wherein the second mixture further includes at least one algaecidal material.

## EVIDENCE APPENDIX

The evidence relied upon by the appellants includes Exhibit A, a Declaration Under Rule 132 of Dr. Keith C Hong. This document was introduced into the record with the Amendment filed by the applicants on January 15, 2007. The evidence relied upon by appellants also includes Exhibit B, Chapter 4 of D. Rhodes, Clay and Glazes for the Potter (Chilton Book Company, Radnor, PA, 1973). This document was introduced into the record with the Amendment filed by the applicants on June 14, 2007.

# **EVIDENCE APPENDIX**

## **EXHIBIT A**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re patent  
appln. of : Keith C. Hong, et al.

Appln. No: 10/600,847

Filed: June 20, 2003

For: **ALGAE RESISTANT ROOFING  
GRANULES WITH CONTROLLED  
ALGAECIDE LEACHING RATES,  
ALGAE RESISTANT SHINGLES, AND  
PROCESS FOR PRODUCING SAME**

Group Art  
Unit: 1762

Examiner: Elena Tsoy

Docket No: 008-02

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Mail Stop Amendment  
Commissioner of Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**DECLARATION UNDER RULE 132 (37 C.F.R. § 1.132)**

As an inventor of the subject matter claimed in the above-referenced patent application, I declare the following:

1. My education and experience are as follows: I hold a B.S. degree in Chemistry from Illinois State University, an M.S. degree in Chemistry from the University of Wisconsin and a Ph.D. degree in Materials Science & Engineering from Massachusetts Institute of Technology. Since 1999, I have been employed by CertainTeed Corporation as a chemist in the area of roofing products, including roofing products containing mineral roofing granules.
2. I have reviewed the Examiner's Action mailed August 14, 2006 in the above-identified patent application and United States Patents 3,528,842 ("Skadulis") and 4,378,408 ("Joedicke '408").

3. As the Examiner correctly notes, Joedicke '408 discloses the addition of gas-forming compounds such as hydrogen peroxide and sodium perborate to a coating composition containing a pigment such as titanium dioxide to greatly enhance film opacity and afford significant pigment reductions, particularly titanium dioxide in whites, where the coating composition is intended to be used in coatings on roofing granules, by undergoing chemical and/or thermal decomposition to gaseous products early in the film drying process and resulting in the uniform distribution of microscopic light-scattering microvoids (i.e. gas-forming particles throughout the film). The Examiner also correctly observes that Joedicke discloses that granules may be coated with multiple coats with any desired amount of the coating material and that the gas forming compound may be used in any one or more of the coatings.

4. As presently claimed, the present invention requires that cuprous oxide be included in the coating composition as an algacide. However, when the coating composition is "cured" at an elevated temperature, the cuprous oxide confers a dark brown color on the granules.

For example, color readings were taken for the colored algae-resistant granules produced following the procedure of Example 6 of the application, using a HunterLab XE spectrometer. The results were  $L^*=23.09$ ;  $a^*=4.30$ ; and  $b^*=2.68$ . With an  $L^*$  value of 23.09, these are very dark colored materials, and pigment reduction would not be practical.

5. Commercial algae-resistant granules are typically gray in color, reflecting the use of carbon black in the coating compositions. Material Safety Data Sheets for two typical commercial algae resistant roofing granules are appended hereto as Exhibits A and B, and show the presence of carbon black in each.

Color readings were taken for the commercial algae-resistant granules referenced in the MSDS sheets in Exhibit A and B. The results are as follows:

CertainTeed (Gads Hill GH-71 AR granules):  $L^*=32.1$ ;  $a^*=3.38$ ; and  $b^*=6.69$

3M (Little Rock LR-700 AR granules):  $L^*=35.6$ ;  $a^*=1.93$ ; and  $b^*=5.02$

Based on the  $L^*$  values, these are both very dark granules.

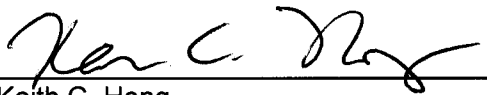
6. One of ordinary skill in the art would not be motivated to add a void-forming material such as hydrogen peroxide or sodium perborate to the inner coating composition material in the process of the present invention, simply because increasing the "opacity" of the coating composition would require additional pigment, rather than less as in the case of white or light-colored materials, and would not improve the appearance of the granules.

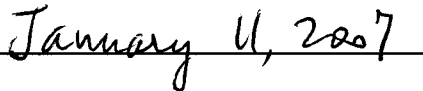
7. With respect to the Examiner's comment in Paragraph 5 of the Examiner's Action that U.S. Patent 4,378,408 ("Joedicke '408") teaches that roofing granules may be coated in multiple coats with any desired amount of coating material and gas-forming compound may be used in any one of multiple coatings to greatly enhance film opacity and afford significant pigment reductions, particularly  $TiO_2$ , in whites (referencing column 5, lines: 38-41), in my opinion one of ordinary skill in this art would have a different understanding of Joedicke '408's teaching. In particular, one of ordinary skill in the art would understand that the effectiveness of microvoids created by gas-forming compounds such as sodium perborate in enhancing the opacity of a multiply layer coating would depend on several parameters, including (1) the specific layer in which the microvoids were created, (2) the composition of the microvoid-carrying layer, (3) the existence of one or more layers exterior to the microvoid-carrying layer and their respective compositions. Thus, while the presence of microvoids in an interior layer coated with a clear, pigment-exterior layer could contribute significantly to the opacity of the entire composition, to the extent the exterior layer or layers includes pigments, the contribution to the opacity of the entire coating composition from microvoids present in interior layers becomes correspondingly less significant. The pigmented outer layer or

layers mask or hide the inner layer, so that light scattering is diminished or extinguished entirely.

8. One of ordinary skill the art would also understand that while light colored coating compositions may be improved by the presence of microvoids, similar improvement is not to be expected in the case of dark colored coating compositions, which tend to absorb light rather than reflect light. On the contrary, one of ordinary skill in the art would understand the adding light-scattering microvoids to a coating composition having a dark color would tend to work against the colored pigment, by lightening the coating, thus requiring more pigment to achieve a desired color, rather than less as in the case of a light-colored coating composition, such as a white coating composition pigmented with titanium dioxide.

9. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

  
\_\_\_\_\_  
Keith C. Hong

  
\_\_\_\_\_  
Date

# **EXHIBIT A**

# Material Safety Data Sheet

Material Name: CertainTeed AR Granules

ID: CT10070

## \*\*\* 1 - CHEMICAL PRODUCT AND COMPANY IDENTIFICATION \*\*\*

**PRODUCT/TRADE NAME:** Artificially colored mineral roofing granules.

**CAS No:** None

**Common Name** Roofing Shingles

**Product Use:** As algae resistant roofing granules on roofing shingles only

### Manufacturer Information

CertainTeed Corporation  
Rt. 2, Highway 49 N  
Piedmont, MO 63957

Phone: 573-223-7554

### Distributor/Contact Information

Distributor's Product Name: 71 AR Roofing Granules Distributor's Product Code: GH 71 AR

CertainTeed Corporation  
Rt. 2, Highway 49 N  
Piedmont, MO 63957

Phone: 573-223-7554

## \*\*\* 2 - COMPOSITION/INFORMATION ON INGREDIENTS \*\*\*

CAS #	Component	Percent
Not Available	Rhyolite rock	85.7
<b>The following component is present in Rhyolite Rock:</b>		
14808-60-7	Quartz (crystalline silica)	15-30
<b>The remaining composition is as follows:</b>		
1317-39-1	Copper oxide	3-8
1332-58-7	Kaolin clay	4-6
1344-09-8	Soda glass	2-4
64742-52-5	Naphthenic oil	0-0.9
1308-38-9	Chromium (III) oxide	0-0.9
1314-13-2	Zinc oxide	0-0.9
68187-51-9	Zinc Ferrite	0-0.9
1333-86-4	Carbon black	0-0.9
13463-67-7	Titanium dioxide	0-0.9

### Component Information/Information on Non-Hazardous Components

#### A: General Product Information

This product is considered hazardous under 29 CFR 1910.1200 (Hazard Communication).

\* Natural Slate granules are a mixture of minerals including quartz.

#### B: Component Exposure Limits

##### Quartz (crystalline silica) (14808-60-7)

ACGIH: 0.05 mg/m3 TWA (respirable fraction)

OSHA: 0.1 mg/m3 TWA (respirable dust)

NIOSH: 0.05 mg/m3 TWA (respirable dust)

##### Kaolin clay (1332-58-7)

ACGIH: 2 mg/m3 TWA (respirable fraction, particulate matter containing no asbestos and < 1% crystalline silica)

OSHA: 10 mg/m3 TWA (total dust); 5 mg/m3 TWA (respirable fraction)

NIOSH: 10 mg/m3 TWA (total dust); 5 mg/m3 TWA (respirable dust)

# Material Safety Data Sheet

Material Name: CertainTeed AR Granules

ID: CT10070

## Zinc oxide (1314-13-2)

ACGIH: 2 mg/m3 TWA (respirable fraction)  
10 mg/m3 STEL (respirable fraction)  
OSHA: 5 mg/m3 TWA (fume); 10 mg/m3 TWA (total dust); 5 mg/m3 TWA (respirable fraction)  
10 mg/m3 STEL (fume)  
NIOSH: 5 mg/m3 TWA (dust and fume)  
10 mg/m3 STEL (fume)  
15 mg/m3 Ceiling (dust)

## Carbon black (1333-86-4)

ACGIH: 3.5 mg/m3 TWA  
OSHA: 3.5 mg/m3 TWA  
NIOSH: 3.5 mg/m3 TWA; 0.1 mg/m3 TWA (as PAH, carbon black in presence of polycyclic aromatic hydrocarbons)

## Titanium dioxide (13463-67-7)

ACGIH: 10 mg/m3 TWA  
OSHA: 10 mg/m3 TWA (total dust)

### \*\*\* 3 - HAZARDS IDENTIFICATION \*\*\*

#### Emergency Overview

Product is green, solid granules, typically 0.02 to 0.100 inches in size. Product is an algicide. May cause mechanical eye, respiratory and skin irritation. This product contains a carcinogen.

#### NFPA Ratings: Health: 1 Fire: 0 Reactivity: 0

Hazard Scale: 0 = Minimal 1 = Slight 2 = Moderate 3 = Serious 4 = Severe

#### HMIS Ratings: Health: 1\* Fire: 0 Physical Hazard: 0 Pers. Prot.: gloves and safety glasses with side shields

Hazard Scale: 0 = Minimal 1 = Slight 2 = Moderate 3 = Serious 4 = Severe \* = Chronic hazard

#### Summary:

Material may irritate skin and eyes on contact or respiratory system if dust or fume is inhaled.

#### Routes of Entry:

Inhalation, skin, and eye contact.

#### Acute Inhalation:

Dusts of this product may cause mechanical irritation of the nose, throat, and respiratory tract. Inhalation of dusts of this product may cause metal fume fever, hemolysis of the red blood cells and injury to the liver, lungs, kidneys and pancreas. Inhalation of petroleum distillate vapors can cause drowsiness, headache and nausea. Ingestion may cause vomiting, gastric pain, dizziness, anemia, cramps, convulsions, shock, coma and death.

#### Chronic Inhalation:

Long term exposure to airborne particles may cause lung damage including a risk of cancer. See Section 11: Toxicological Information.

#### Acute Skin Contact:

Contact with the skin may result in mechanical irritation characterized by itching or redness.

#### Chronic Skin Contact:

None identified.

#### Acute Eye Contact:

Contact with the eye may result in mechanical irritation characterized by itching or redness.

#### Chronic Eye Contact:

None identified.

#### Acute Ingestion:

Ingestion of this product is unlikely. However, ingestion of product may produce gastrointestinal irritation and disturbances.

#### Chronic Ingestion:

None identified.

# Material Safety Data Sheet

Material Name: CertainTeed AR Granules

ID: CT10070

## Carcinogenicity

### A: General Product Information

The International Agency for Research on Cancer (IARC) has classified crystalline silica as a Group 1 substance, carcinogenic to humans. This classification is based on the findings of laboratory animal studies (inhalation, injection, and implantation) and epidemiology studies that were considered sufficient for carcinogenicity. Several studies have been conducted to determine the risk of cancer to workers exposed to dusts which contain crystalline silica. However, these studies did not consider other factors or elements that workers may be exposed to. Therefore, the causes of the excess deaths due to cancer could not be precisely determined. Further studies are being conducted to determine the risk of cancer when working with crystalline silica products. Excessive exposure to crystalline silica can cause silicosis, a non-cancerous lung disease. Respirable crystalline silica has been classified by the National Toxicology Program (NTP) as a substance which may reasonably be anticipated to be a carcinogen.

### B: Component Carcinogenicity

#### Quartz (crystalline silica) (14808-60-7)

ACGIH: A2 - Suspected Human Carcinogen

NIOSH: potential occupational carcinogen

IARC: Monograph 68, 1997 (inhaled in the form of quartz or cristobalite from occupational sources)  
(Group 1 (carcinogenic to humans))

#### Kaolin clay (1332-58-7)

ACGIH: A4 - Not Classifiable as a Human Carcinogen

#### Carbon black (1333-86-4)

ACGIH: A4 - Not Classifiable as a Human Carcinogen

NIOSH: potential occupational carcinogen (in presence of polycyclic aromatic hydrocarbons)

IARC: Monograph 65, 1996 (Group 2B (possibly carcinogenic to humans))

#### Titanium dioxide (13463-67-7)

ACGIH: A4 - Not Classifiable as a Human Carcinogen

NIOSH: potential occupational carcinogen

IARC: Monograph 47, 1989 (Group 3 (not classifiable))

## Mutagenicity:

None identified.

## Teratogenicity:

None identified.

## Reproductive Toxicity:

None identified.

## Toxicological Synergistic Products:

None identified.

## Medical Conditions Aggravated by Exposure:

Respiratory or skin conditions that are aggravated by mechanical irritants may be at an increased risk for worsening from exposure to dust.

## \*\*\* 4 - FIRST AID MEASURES \*\*\*

### Inhalation:

Remove to fresh air. Drink water to clear throat, and blow nose to remove dust. If symptoms persist, get medical attention.

### Skin:

For skin contact, wash immediately with soap and water. If irritation persists, get medical attention.

### Eyes:

Flush eyes with large amounts of water for 5-15 minutes. If irritation develops, or persists, seek medical attention.

### Ingestion:

Ingestion is unlikely under normal conditions. If granules are swallowed, seek medical attention or advice. Do not induce vomiting.

# Material Safety Data Sheet

Material Name: CertainTeed AR Granules

ID: CT10070

## Fires:

Move to fresh air. Administer oxygen and get help.

### \*\*\* 5 - FIRE FIGHTING MEASURES \*\*\*

## Extinguishing Media:

Use methods for the surrounding fire. Dry chemical, foam and water fog.

## Special Fire-Fighting Procedures:

Firefighters should wear full protective clothing including self contained breathing apparatus.

## Hazardous Decomposition Products

Upon decomposition, this product emits carbon monoxide, carbon dioxide and/or low molecular weight hydrocarbons.

**Flash Point:** Not available

**Upper Flammable Limit (UFL):** Not determined

**Auto Ignition:** Not available

**Rate of Burning:** Not available

## Unusual Fire and Explosion Hazards:

Product contains a small percentage of petroleum distillate that has a flashpoint of 149°F and may be combustible.

**Method Used:**

**Lower Flammable Limit (LFL):** Not determined

**Flammability Classification:** Non-combustible

### \*\*\* 6 - ACCIDENTAL RELEASE MEASURES \*\*\*

## Spills:

Pick up large pieces. Scoop up material and put into a suitable container for disposal as a non-hazardous waste.

## Accidental or Unplanned Releases:

None necessary.

## Personal Protective Equipment:

See Section 8 of this MSDS for recommended PPE.

### \*\*\* 7 - HANDLING AND STORAGE \*\*\*

## Handling:

For industrial use only as surfacing of roofing shingles. Avoid generation of dusts. Control dusting with engineering practices or wear personal protective equipment including respirator. Wash thoroughly after handling. Avoid contact with skin and eyes. Use good general housekeeping practices to prevent accumulation of dust in work area.

## Storage:

Store away from water, oxidizing agents, and acids.

### \*\*\* 8 - EXPOSURE CONTROL / PERSONAL PROTECTION \*\*\*

## Work Practices and Engineering Controls:

Ventilation should effectively remove and prevent buildup of any vapor/mist/fume/dust generated from the handling of this product.

## PERSONAL PROTECTIVE EQUIPMENT

### Eye:

Safety glasses with sideshields.

### Respirators:

If ventilation is not sufficient to effectively prevent buildup of fumes or dusts, appropriate NIOSH/MSHA respiratory protection must be provided.

### Skin:

Leather or cotton gloves should be worn to prevent skin contact and irritation. Normal work clothing (long sleeved shirts and long pants) is recommended.

### Other Protection:

Protective equipment should be provided as necessary to prevent irritation to the throat, eyes, and skin, and to keep exposures below the applicable exposure limits identified in Section 8.

# Material Safety Data Sheet

Material Name: CertainTeed AR Granules

ID: CT10070

## \*\*\* 9 - PHYSICAL AND CHEMICAL PROPERTIES \*\*\*

**Appearance:** green  
**Physical State:** solid granules  
**Vapor Pressure:** Not applicable  
**Boiling Point:** Not applicable  
**Solubility (H2O):** Negligible  
**Viscosity:** Not applicable

**Odor:** slightly oily odor  
**pH:** 7.0 - 10.0  
**Vapor Density:** Not applicable  
**Melting Point:** >3000°F  
**Specific Gravity:** 2.5 - 2.8

## \*\*\* 10 - REACTIVITY \*\*\*

### Stability:

This is a stable material.

### Corrosivity:

Not applicable

### Incompatibility:

Strong oxidizing agents, reducing agents, strong acids and alkalies. Hydrofluoric acid will dissolve base rock.

### Reactivity:

Not applicable

### Reactivity with water:

None.

### Hazardous Decomposition Products:

Upon decomposition, this product emits oxides, fumes, and/or low molecular weight hydrocarbons.

### Explosion:

None expected.

### Hazardous Polymerization

Will not occur.

## \*\*\* 11 - TOXICOLOGICAL INFORMATION \*\*\*

Overexposure to dusts may result in pneumoconiosis, a lung disease due to permanent deposition of substantial amounts of particulate matter in the lungs. Chronic inhalation of kaolin dust can cause kaolinosis, a particular type of pneumoconiosis characterized by positive x-ray findings and mild reductions in pulmonary function. Excessive inhalation of respirable crystalline silica dust may cause a progressive, disabling and sometimes fatal lung disease called silicosis. Symptoms of silicosis include cough, shortness of breath, wheezing, non-specific chest illness and reduced pulmonary function.

### Acute Effects:

#### A: General Product Information

The primary acute health effects of this product include mechanical irritation of the skin, eyes and throat as a result of contact with material.

Copper oxide, a component of this product, may cause metal fume fever, hemolysis of the red blood cells and injury to the liver, lungs, kidneys and pancreas. Ingestion may also cause vomiting, gastric pain, dizziness, anemia, cramps, convulsions, shock, coma and death.

#### B: Component Analysis - LD50/LC50

##### Copper oxide (1317-39-1)

Oral LD50 Rat: 470 mg/kg

##### Zinc oxide (1314-13-2)

Oral LD50 Mouse: 7950 mg/kg

##### Carbon black (1333-86-4)

Oral LD50 Rat: >15400 mg/kg; Dermal LD50 Rabbit: >3 g/kg

# Material Safety Data Sheet

Material Name: CertainTeed AR Granules

ID: CT10070

## Chronic Effects:

This product contains crystalline silica. Crystalline silica is considered hazardous by inhalation. Prolonged and repeated inhalation of respirable crystalline silica can cause silicosis, a chronic lung disease characterized by fibrosis and scarring of the lung tissue resulting in a decrease in lung function, breathlessness, wheezing, coughing and sputum production. Short term overexposures to extremely high concentrations of respirable crystalline silica can produce acute silicosis. Acute silicosis is a disease that can rapidly progress within months of initial overexposure and reportedly has caused death within 1 to 2 years.

## \*\*\* 12 - ECOLOGICAL INFORMATION \*\*\*

### Ecotoxicity

#### A: General Product Information

No additional information available.

#### B: Component Analysis - Ecotoxicity - Aquatic Toxicity

No ecotoxicity data are available for this product's components.

### Environmental Fate

No information available.

## \*\*\* 13 - WASTE DISPOSAL CONSIDERATIONS \*\*\*

### US EPA Waste Number & Descriptions

#### A: General Product Information

This product, as supplied, is not regulated as a hazardous waste by the U.S. Environmental Protection Agency (EPA) under Resource Conservation and Recovery Act (RCRA) regulations. Comply with state and local regulations for disposal. If you are unsure of the regulations, contact your local Public Health Department, or the local office of the EPA.

#### B: Component Waste Numbers

No EPA Listed Waste Numbers are being shown for this product's components.

### Disposal Instructions

Dispose of waste material according to Local, State, Federal, and Provincial Environmental Regulations.

## \*\*\* 14 - TRANSPORTATION INFORMATION \*\*\*

### US DOT Information

**Shipping Name:** Not regulated for transportation.

## \*\*\* 15 - REGULATORY INFORMATION \*\*\*

### US Federal Regulations

#### A: General Product Information

No information available.

#### B: Clean Air Act

This product is not manufactured with, nor does it contain any Class I ozone depleting chemicals as defined by EPA in Title VI of Clean Air Act Amendments of 1990 (40 CFR Part 82-Production Of Stratospheric Ozone).

This product is not subject to Section 112(r) of the Clean Air Act.

#### C: CERCLA

None of the components of this product are listed under CERCLA (40 CFR 302.4) and present in the material at an amount exceeding the Reportable Quantity (RQ).

#### D: SARA Title III Regulations:

None of this product's components are listed under SARA Section 302 (40 CFR 355 Appendix A), and/or SARA Section 313 (40 CFR 372.65).

**Acute Health:** No **Chronic Health:** Yes **Fire:** No **Pressure:** No **Reactive:** No

### State Regulations

#### A: General Product Information

Other state regulations may apply. Check individual state requirements.

# Material Safety Data Sheet

Material Name: CertainTeed AR Granules

ID: CT10070

## B: Component Analysis - State

The following components appear on one or more of the following state hazardous substances lists:

Component	CAS	CA	MA	MN	NJ	PA	RI
Quartz (crystalline silica)	14808-60-7	No	Yes	Yes	Yes	Yes	No
Kaolin clay	1332-58-7	No	Yes	Yes	No	Yes	Yes
Chromium (III) oxide	1308-38-9	No	Yes	No	Yes	No	No
Zinc oxide	1314-13-2	Yes	Yes	Yes	Yes	Yes	Yes
Carbon black	1333-86-4	Yes	Yes	Yes	Yes	Yes	Yes
Titanium dioxide	13463-67-7	No	Yes	Yes	Yes	Yes	Yes

## C: California Safe Drinking Water and Toxics Enforcement Act (Proposition 65)

The following statement(s) are provided under the California Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65):

WARNING! This product contains a chemical known to the state of California to cause cancer.

## Component Analysis - WHMIS IDL

The following components are identified under the Canadian Hazardous Products Act Ingredient Disclosure List:

Component	CAS #	Minimum Concentration
Quartz (crystalline silica)	14808-60-7	1 % (English Item 1406, French Item 1491)
Copper oxide	1317-39-1	1 % (English Item 437, French Item 1307)

## Additional Regulatory Information

### A: General Product Information

No information available.

### B: Component Analysis - Inventory

Component	CAS #	TSCA	DSL	EINECS
Quartz (crystalline silica)	14808-60-7	Yes	Yes	Yes
Copper oxide	1317-39-1	Yes	Yes	Yes
Kaolin clay	1332-58-7	Yes	Yes	No
Soda glass	1344-09-8	Yes	Yes	Yes
Naphthenic oil	64742-52-5	Yes	Yes	Yes
Chromium (III) oxide	1308-38-9	Yes	Yes	Yes
Zinc oxide	1314-13-2	Yes	Yes	Yes
Zinc Ferrite	68187-51-9	Yes	Yes	Yes
Carbon black	1333-86-4	Yes	Yes	Yes
Titanium dioxide	13463-67-7	Yes	Yes	Yes

## \*\*\* 16 - ADDITIONAL COMMENTS \*\*\*

### Other Information

Reasonable care has been taken in the preparation of this information, but the manufacturer makes no warranty of merchantability or any other warranty, expressed or implied, with respect to this information. The manufacturer makes no representations and assumes no liability for any direct, incidental or consequential damages resulting from its use.

### MSDS History

MSDS Revision Summary:

Date:

11/04/2004

MSDS No:

CT10070-1

Comments:

New MSDS

### Key/Legend

CFR = Code of Federal Regulations;

EPA = Environmental Protection Agency;

TSCA = Toxic Substance Control Act;

## Material Safety Data Sheet

**Material Name: CertainTeed AR Granules**

**ID: CT10070**

ACGIH = American Conference of Governmental Industrial Hygienists;  
IARC = International Agency for Research on Cancer;  
NIOSH = National Institute for Occupational Safety and Health;  
NTP = National Toxicology Program;  
OSHA = Occupational Safety and Health Administration;  
NFPA = National Fire Protection Association;  
HMIS = Hazardous Material Identification System;  
CERCLA = Comprehensive Environmental Response, Compensation and Liability Act;  
SARA = Superfund Amendments and Reauthorization Act;  
DSL = Canadian Domestic Substance List;  
EINECS = European Inventory of New and Existing Chemical Substances;  
RCRA = Resource Conservation and Recovery Act

This is the end of MSDS # CT10070

## **EXHIBIT B**



## Material Safety Data Sheet

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### SECTION 1: PRODUCT AND COMPANY IDENTIFICATION

**PRODUCT NAME:** 3M Brand Copper Roofing Granules - LR7000, LR7022, LR7050 & LR7070 (Little Rock, AR)

**MANUFACTURER:** 3M

**DIVISION:** Industrial Mineral Division

**ADDRESS:** 3M Center  
St. Paul, MN 55144-1000

EMERGENCY PHONE: 1-800-364-3577 or (651) 737-6501 (24 hours)

**Issue Date:** 10/04/2006

**Supersedes Date:** 10/02/2006

**Document Group:** 11-3796-7

#### Product Use:

Intended Use: ROOFING GRANULES FOR ROOFING SHINGLES

### SECTION 2: INGREDIENTS

<u>Ingredient</u>	<u>C.A.S. No.</u>	<u>% by Wt</u>
Nepheline Syenite (composition varies naturally; typically contains feldspars, nepheline, analcite, pyroxene, amphibole, magnetite, and biotite)	68476-25-5	90 - 95
Copper Oxide	1317-39-1	4 - 8
Ceramic Coating	Trade Secret	3 - 7
Inorganic Pigments	Mixture	0.1 - 2
Quartz (a component of Nepheline Syenite)	14808-60-7	< 0.9
Carbon Black	1333-86-4	< 0.5
Chromium (III) Oxide	1308-38-9	< 0.5
Oil	64742-52-5	< 0.5

### SECTION 3: HAZARDS IDENTIFICATION

#### 3.1 EMERGENCY OVERVIEW

**Specific Physical Form:** Granules

**Odor, Color, Grade:** Slightly oily odor, Typical particle size 0.84-2.0 mm

**General Physical Form:** Solid

**Immediate health, physical, and environmental hazards:** Granules are not respirable. Dust generated during handling may contain

respirable material. Contains a chemical or chemicals which can cause cancer.

## 3.2 POTENTIAL HEALTH EFFECTS

### Eye Contact:

Mechanical eye irritation: Signs/symptoms may include pain, redness, tearing and corneal abrasion.

### Skin Contact:

Mechanical Skin irritation: Signs/symptoms may include abrasion, redness, pain, and itching.

### Inhalation:

Upper Respiratory Tract Irritation: Signs/symptoms may include cough, sneezing, nasal discharge, headache, hoarseness, and nose and throat pain.

Prolonged or repeated exposure, above recommended guidelines, may cause:

Silicosis: Signs/symptoms may include breathlessness, weakness, chest pain, persistent cough, increased amounts of sputum, and heart disease.

### Ingestion:

Gastrointestinal Irritation: Signs/symptoms may include abdominal pain, nausea, diarrhea and vomiting.

### Carcinogenicity:

Contains a chemical or chemicals which can cause cancer.

<u><b>Ingredient</b></u>	<u><b>C.A.S. No.</b></u>	<u><b>Class Description</b></u>	<u><b>Regulation</b></u>
Carbon Black	1333-86-4	Group 2B	International Agency for Research on Cancer
Quartz (a component of Nepheline Syenite)	14808-60-7	Group 1	International Agency for Research on Cancer
Quartz (a component of Nepheline Syenite)	14808-60-7	Known human carcinogen	National Toxicology Program Carcinogens

## SECTION 4: FIRST AID MEASURES

### 4.1 FIRST AID PROCEDURES

The following first aid recommendations are based on an assumption that appropriate personal and industrial hygiene practices are followed.

**Eye Contact:** Flush eyes with large amounts of water. If signs/symptoms persist, get medical attention.

**Skin Contact:** Wash affected area with soap and water. If signs/symptoms develop, get medical attention.

**Inhalation:** Remove person to fresh air. If signs/symptoms develop, get medical attention.

**If Swallowed:** Do not induce vomiting. Give victim two glasses of water. Never give anything by mouth to an unconscious person. Get immediate medical attention.

## SECTION 5: FIRE FIGHTING MEASURES

### 5.1 FLAMMABLE PROPERTIES

Autoignition temperature	<i>Not Applicable</i>
Flash Point	<i>Not Applicable</i>
Flammable Limits - LEL	<i>Not Applicable</i>

Flammable Limits - UEL

*Not Applicable*

## 5.2 EXTINGUISHING MEDIA

Material will not burn.

## 5.3 PROTECTION OF FIRE FIGHTERS

**Special Fire Fighting Procedures:** Wear full protective equipment (Bunker Gear) and a self-contained breathing apparatus (SCBA).

**Unusual Fire and Explosion Hazards:** Not applicable.

**Note:** See STABILITY AND REACTIVITY (SECTION 10) for hazardous combustion and thermal decomposition information.

## SECTION 6: ACCIDENTAL RELEASE MEASURES

**Accidental Release Measures:** Observe precautions from other sections. Call 3M- HELPS line (1-800-364-3577) for more information on handling and managing the spill. Ventilate the area with fresh air. Reclaim undamaged product. Collect as much of the spilled material as possible. Clean up residue. Place in a closed container approved for transportation by appropriate authorities.

**In the event of a release of this material, the user should determine if the release qualifies as reportable according to local, state, and federal regulations.**

## SECTION 7: HANDLING AND STORAGE

### 7.1 HANDLING

Do not eat, drink or smoke when using this product. Wash exposed areas thoroughly with soap and water. For industrial or professional use only. Use general dilution ventilation and/or local exhaust ventilation to control airborne exposures to below Occupational Exposure Limits. If ventilation is not adequate, use respiratory protection equipment. 3M does not recommend material handling methods that could damage the coating or base mineral. In particular, roofing granules should not be conveyed pneumatically, via screw conveyors, or used as a sand blasting media. These uses can cause coating and base mineral attrition which may lead to increased levels of dust generation.

### 7.2 STORAGE

Not applicable.

## SECTION 8: EXPOSURE CONTROLS/PERSONAL PROTECTION

### 8.1 ENGINEERING CONTROLS

Use with appropriate local exhaust ventilation. Provide local exhaust ventilation at transfer points.

### 8.2 PERSONAL PROTECTIVE EQUIPMENT (PPE)

#### 8.2.1 Eye/Face Protection

The following eye protection(s) are recommended: Safety Glasses with side shields.

#### 8.2.2 Skin Protection

Gloves not normally required. Avoid prolonged or repeated skin contact.

#### 8.2.3 Respiratory Protection

Select one of the following NIOSH approved respirators based on airborne concentration of contaminants and in accordance with OSHA regulations: Half mask R95 particulate respirator, Half mask or full facepiece air-purifying respirator with N100 particulate filters, Half facepiece or fullface air-purifying respirator with P100 particulate filters, Half facepiece or fullface air-purifying respirator with P95 particulate filters, Half facepiece or fullface air-purifying respirator with N95 particulate filters. Consult the current 3M Respiratory Selection Guide for additional information or call 1-800-243-4630 for 3M technical assistance.

#### 8.2.4 Prevention of Swallowing

Do not eat, drink or smoke when using this product. Wash exposed areas thoroughly with soap and water. Wash hands after handling and before eating.

### 8.3 EXPOSURE GUIDELINES

<u><b>Ingredient</b></u>	<u><b>Authority</b></u>	<u><b>Type</b></u>	<u><b>Limit</b></u>	<u><b>Additional Information</b></u>
Carbon Black	ACGIH	TWA	3.5 mg/m3	Table A4
Carbon Black	CMRG	TWA	0.5 mg/m3	
Carbon Black	OSHA	TWA	3.5 mg/m3	Table Z-1
CHROMIUM (III) COMPOUNDS	ACGIH	TWA, as Cr	0.5 mg/m3	Table A4
CHROMIUM (III) COMPOUNDS	OSHA	TWA, as Cr	0.5 mg/m3	Table Z-1
COPPER COMPOUNDS	ACGIH	TWA, as Cu dust or mist	1 mg/m3	
COPPER COMPOUNDS	OSHA	TWA, as dust or mist	1 mg/m3	Table Z-1A
Quartz (a component of Nepheline Syenite)	ACGIH	TWA, respirable	0.025 mg/m3	Table A2
Quartz (a component of Nepheline Syenite)	OSHA	TWA, respirable	0.1 mg/m3	Table Z-1A

#### SOURCE OF EXPOSURE LIMIT DATA:

ACGIH: American Conference of Governmental Industrial Hygienists

CMRG: Chemical Manufacturer Recommended Guideline

OSHA: Occupational Safety and Health Administration

AIHA: American Industrial Hygiene Association Workplace Environmental Exposure Level (WEEL)

## SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES

<b>Specific Physical Form:</b>	Granules
<b>Odor, Color, Grade:</b>	Slightly oily odor, Typical particle size 0.84-2.0 mm
<b>General Physical Form:</b>	Solid
<b>Autoignition temperature</b>	<i>Not Applicable</i>
<b>Flash Point</b>	<i>Not Applicable</i>
<b>Flammable Limits - LEL</b>	<i>Not Applicable</i>
<b>Flammable Limits - UEL</b>	<i>Not Applicable</i>
<b>Specific Gravity</b>	2.5 - 2.6 [ <i>Ref Std: WATER=1</i> ]
<b>Melting point</b>	<i>Not Applicable</i>
<b>Solubility in Water</b>	Negligible
<b>Percent volatile</b>	Nil

## SECTION 10: STABILITY AND REACTIVITY

**Stability:** Stable.

**Materials and Conditions to Avoid:** None known

**Hazardous Polymerization:** Hazardous polymerization will not occur.

### Hazardous Decomposition or By-Products

Substance

None known.

Condition

Not Specified

## SECTION 11: TOXICOLOGICAL INFORMATION

Please contact the address listed on the first page of the MSDS for Toxicological Information on this material and/or its components.

## SECTION 12: ECOLOGICAL INFORMATION

### ECOTOXICOLOGICAL INFORMATION

Not determined.

### CHEMICAL FATE INFORMATION

Not determined.

## SECTION 13: DISPOSAL CONSIDERATIONS

**Waste Disposal Method:** Reclaim if feasible. Since regulations vary, consult applicable regulations or authorities before disposal.

NOTE: Waste is considered a California hazardous waste (See REGULATORY INFORMATION).

**EPA Hazardous Waste Number (RCRA):** Not regulated

Since regulations vary, consult applicable regulations or authorities before disposal.

## SECTION 14: TRANSPORT INFORMATION

**ID Number(s):**

98-0111-1209-5, 98-0111-1215-2, 98-0111-1243-4, 98-0111-1255-8, 98-0111-1256-6, 98-0111-1398-6, 98-0111-1512-2, 98-0111-1765-6, 98-0111-1766-4, 98-0111-1767-2, 98-0111-1768-0, 98-0111-1769-8, 98-0111-1770-6, 98-0111-1771-4, 98-0111-1772-2, 98-0111-1797-9, 98-0111-1798-7, 98-0111-1799-5, 98-0111-1800-1, 98-0111-1828-2

Please contact the emergency numbers listed on the first page of the MSDS for Transportation Information for this material.

## SECTION 15: REGULATORY INFORMATION

### US FEDERAL REGULATIONS

Contact 3M for more information.

**311/312 Hazard Categories:**

Fire Hazard - No    Pressure Hazard - No    Reactivity Hazard - No    Immediate Hazard - Yes    Delayed Hazard - Yes

**Section 313 Toxic Chemicals subject to the reporting requirements of that section and 40 CFR part 372 (EPCRA):**

<b><u>Ingredient</u></b>	<b><u>C.A.S. No</u></b>	<b><u>% by Wt</u></b>
Copper Oxide (COPPER COMPOUNDS (EPCRA 313))	1317-39-1	4 - 8

#### FIFRA

<b><u>Status</u></b>	<b><u>Registration Number</u></b>
Registered	10350-57

### STATE REGULATIONS

Contact 3M for more information.

### CALIFORNIA PROPOSITION 65

<b><u>Ingredient</u></b>	<b><u>C.A.S. No.</u></b>	<b><u>Classification</u></b>
Carbon Black	1333-86-4	**Carcinogen
SILICA, CRYSTALLINE (AIRBORNE PARTICLES OF RESPIRABLE SIZE)	NONE	**Carcinogen

\*\* WARNING: contains a chemical which can cause cancer.

### CHEMICAL INVENTORIES

The components of this product are in compliance with the chemical notification requirements of TSCA.

Contact 3M for more information.

### INTERNATIONAL REGULATIONS

Contact 3M for more information.

### ADDITIONAL INFORMATION

#### 3M COPPER GRANULES

Built-in control of algae to maintain the beauty of roofing shingles

#### ACTIVE INGREDIENT

Cuprous oxide	6.0%
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<b>OTHER INGREDIENTS</b>	94.0%
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Total	100.0%
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(

**KEEP OUT OF REACH OF CHILDREN**

**CAUTION**

#### STORAGE AND DISPOSAL

Do not contaminate water, food, or feed by storage and disposal.

Pesticide Storage:

Store under ambient conditions.

Pesticide Disposal:

Wastes resulting from the use of this product may be disposed of on-site or at an approved waste disposal facility.

Pesticide Container Disposal:

Return empty container for recycling or reuse.

## **DIRECTIONS FOR USE**

It is a violation of Federal Law to use this product in a manner inconsistent with its labeling.

If granules are to be stored prior to (and during) use, a copy of this label must be made readily accessible to employees when they are in their work area(s).

3M Copper Granules contain copper oxide, an effective algacide for inhibiting the growth of blue-green algae that can stain roofing shingles. 3M Copper Granules are treated roofing granules 1-2 mm in diameter made from rock coated with copper oxide and sealed in a ceramic shell. The ceramic shell allows a timed release of copper to provide long-lasting algae control that may extend the useful life of shingles.

3M Copper Granules should be mixed with standard roofing granules at the rate of 5-10% by weight and processed normally during manufacture of the shingles.

## **WARRANTY**

3M warrants that the 3M Copper Granules conforms to the ingredient statement above.

EPA Reg. No. 10350-57

EPA Est. No. 10350-AR-001

EPA Est. No. 10350-WI-002

Net Contents: Bulk shipment; see waybill

3M, St. Paul, MN 55144-1000

## **ADDITIONAL INFORMATION**

California Code of Regulations (CCR) Title 22 hazardous waste for copper. Empty containers could also be considered hazardous waste and should be disposed of according to state and local regulations.

**This MSDS has been prepared to meet the U.S. OSHA Hazard Communication Standard, 29 CFR 1910.1200.**

## **SECTION 16: OTHER INFORMATION**

### **NFPA Hazard Classification**

**Health:** 1 **Flammability:** 0 **Reactivity:** 0 **Special Hazards:** None

National Fire Protection Association (NFPA) hazard ratings are designed for use by emergency response personnel to address the hazards that are presented by short-term, acute exposure to a material under conditions of fire, spill, or similar emergencies. Hazard ratings are primarily based on the inherent physical and toxic properties of the material but also include the toxic properties of combustion or decomposition products that are known to be generated in significant quantities.

Revision Changes: Not Applicable

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**3M MSDSs are available at [www.3M.com](http://www.3M.com)**

# **EVIDENCE APPENDIX**

## **EXHIBIT B**



# CLAY AND GLAZES FOR THE POTTER

*Revised Edition*

DANIEL RHODES

CHILTON BOOK COMPANY RADNOR, PENNSYLVANIA

## CLAY

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# 4 Drying and Firing Clay

## 1. The Process of Drying

Clay, until it is fired and made durable, is a material of little or no practical value. The adobe, or sun-dried brick, is an exception, but no one would maintain that an adobe brick as such was superior to a fired brick. We are interested in clay not so much for what it is in the natural state as for what it may become. By a happy coincidence, clay, which is so plastic and easily shaped, becomes, when fired to red heat or more, a hard and permanent substance.

The discovery that clay will become hard and durable when fired ranks as one of man's most important early finds. The domestic life of primitive man was immeasurably enriched by the possession of fired clay vessels for storing grain, carrying water, cooking, washing, holding food—to say nothing of the ceremonial and purely esthetic uses to which clay objects were put. Any ancient civilization can be gauged by the quantity and the quality of the pottery which

it produced. Clay was no doubt first fired accidentally in a campfire, perhaps in the form of a mud-lined basket. Much early pottery was made in the shape and texture of baskets—a fact which strongly suggests the probability that pottery began as mud smeared on the inside of baskets to make them more water or rodentproof.

When plastic clay dries, it shrinks about 5 percent. Some very plastic clays may shrink as much as 8 percent. Although this shrinkage takes place rather slowly, it creates a problem in completing any object made of plastic clay. When dry clay is moistened, it takes up a surprising quantity of water. Each individual particle of clay holds water like an absorbent pebble, and in between the particles water creates a film. An average clay, to become plastic enough to model, will require about 35 parts of water, by weight, to each 100 parts of clay. Any mass of plastic clay, therefore, is at least one fourth water.

The drying of clay proceeds at a rate

controlled by the humidity of the surrounding atmosphere. When the humidity is 100 percent, nothing dries. But if the humidity of the surrounding air is less than 100 percent, water leaves the clay as a vapor. When the surface of the mass of clay is dried slightly, more water is drawn out from the interior of the mass by capillary attraction. Unless the mass of clay is very thick, drying will proceed quite evenly throughout. If this were not the case, it would be impossible to make objects from plastic clay, because cracks would develop on the dried surface.

The drying of clay is always accompanied by shrinkage. As the film of water between the particles of clay is drawn off by evaporation, the particles draw closer and closer together, thus taking up the space which had been occupied by the water. The cumulative effect of each particle drawing closer to its neighboring particle is the shrinkage of the entire mass. The amount of this drying shrinkage will depend upon the size of the clay particles and on the amount of water which separates them. Those clays having a very fine particle size will shrink more because of the presence of more water-filled interstices which close up. Conversely, more open clays, that is, clays with larger particle size, will shrink less. Drying shrinkage is always related to the grain structure of a clay and, therefore, also to plasticity.

When the water has evaporated from between the clay particles and all the particles are in contact, drying shrinkage is complete. At this stage, which is called the leather-hard state, the clay particles themselves may still be damp and drying will not be complete until this moisture also leaves by evaporation. The drying of the clay particles themselves does not cause any further shrinkage.

The drying shrinkage of a clay may vary depending on how the platelike clay particles have been oriented in the forming process. The clay platelets tend to align themselves at right angles to the force applied to the clay. Linear shrinkage will be less in the direction parallel to the alignment of the platelets than it will be in the direction at right angles to them. Thus when a ball of clay is pounded or pressed to form a sheet or slab, the linear shrinkage across the slab will be less than that of a bar or roll made of the same clay. This variation in shrinkage, although measurable, seldom causes any practical difficulty.

If warping, cracking, or deformation is to be avoided, objects made of plastic clay must be dried slowly and evenly. If one part of a clay object dries more rapidly than another, the unequal shrinkage between the two portions may cause warping or cracking. This may happen, for example, when a clay pot is dried in the sun or in a place where a draft strikes one side. Another familiar example is the tile which curls upward when it dries; the face of the tile, which is exposed to the air, shrinks more rapidly than the back. In the case of objects made from very plastic clays, drying may be a serious problem, not only because of the excessive shrinkage, but because of the tendency of the clay to warp and crack. Handles, spouts, and other appendages may be difficult to attach without subsequent cracking.

Drying is greatly facilitated by the presence in the clay of any sort of nonplastic particles. Such particles tend to take up much less water than clay and are, therefore, more easily dried out. Nonplastic particles also furnish open pores or channels through which moisture can escape toward the surface. Clays which contain a large percentage of nonclay particles, especially if these

*Drying*

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particles are relatively large, are called "open" bodies. When objects are to be made having thick walls or sections, as in some sculptures or terra cottas, open clay bodies are necessarily used. Grog is ordinarily used for this purpose. Grog is clay which has already been fired and then ground to more or less fine particle size. Such a material, of course, having already been dried and fired, undergoes no further shrinkage, and the addition of grog to a clay body will decrease the total shrinkage. Other materials which may also decrease shrinkage and promote rapid drying are flint and feldspar. When a very plastic clay is necessary, as in a clay designed for throwing, the nonplastics must be held to a minimum.

A piece of dried clay will contain more or less free water, as the surrounding atmosphere is, respectively, more or less humid. For this reason drying is actually completed in the kiln. When the temperature of the kiln reaches the boiling point of water, 100° centigrade, all the uncombined water in the clay will have evaporated, and at that point the clay will be completely dry.

Dried clay bodies vary greatly in dry strength. An object made from ball clay, for example, may be six or seven times as strong as one made from Georgia kaolin. The property of dry strength is directly related to particle size, and thus to plasticity; the more plastic a clay is, the more strength it will develop in the dry state.

## 2. Early Stages of Firing—Drying and Water-Smoking

Profound changes occur in clay during firing. A piece of fired clay is quite different both chemically and physically from raw clay. The material, which was

once soft, easily disintegrated, plastic when wet, and without cohesion or strength, becomes, when fired, hard, rocklike, and impervious to water. Clay is actually a relatively indestructible material after it has been fired. Although a piece of pottery will break, its fragments will remain unchanged for thousands of years even when buried in damp soil or when immersed in water.

The first change which firing brings about in clay is a completion of drying. This final drying must be brought about slowly; otherwise the formation of steam within the body of the clay may cause it to burst. This is the familiar explosion in the amateur's kiln which is usually caused by a too rapid advance of heat in the early stages of firing or by pockets of air in the clay. No matter how dry a clay object may seem to be when it is put in the kiln, a considerable amount of water must still be driven off. In the case of large kilns, filled with heavy clay products such as brick or tile, large quantities of water escape from the kiln, and sometimes blowholes are provided in the top of the kiln to let off the water vapor. In smaller kilns the escaping moisture, though present, may not be noticeable. The danger of explosions resulting from steam forming in the object is greatly increased by heavy cross sections or thick-walled objects, and such objects must be fired with great care.

Humidity driers are sometimes used to facilitate safe and rapid drying. The damp clay pieces are heated to nearly 100° in an enclosure which is kept at a humidity of close to 100 percent. Although the clay pieces are heated, no drying occurs. Then the humidity is gradually reduced and the clay pieces, being hot throughout, dry rapidly.

Another version of humidity drying is the practice of "wet firing." Damp

pots, even some taken directly from the wheel, are tightly packed into the kiln. The burners are turned on with the damper partially closed to prevent too much draft through the kiln. The temperature advances rapidly, but the humidity in the kiln rises and thus prevents the pots from breaking from the formation of steam. When the pots reach a temperature approaching 100°, drying proceeds very rapidly and the firing may be continued on a normal schedule. Wet firing is not practical for pieces with thick walls. It is sometimes used in salt glazing. Wet pots, fresh from the wheel, are placed in the kiln and the firing commenced. They are next seen finished and glazed as they come from the completed firing.

The next change which occurs in the firing of clay occurs at about 350°, at which point the chemically combined water of the clay begins to be driven off. This chemically combined water is not to be confused with pore water and water of plasticity, which escapes from the clay during drying. Chemically combined water is a part of the molecular structure of the clay and is unaffected by temperatures below about 350°. It will be noted from the chemical formula of clay that there are two molecules of water to each two molecules of silica and each single molecule of alumina. Expressed as a percentage, this means that clay contains by weight about 14 percent water. When this chemically combined water leaves the clay, enough time must be allowed in firing to prevent the sudden evolution of steam and the possible breaking of the object.

Once a piece of clay has been fired to about 500°, it will be completely dehydrated, and it will no longer slake or disintegrate in water. It will also have lost its plasticity. Although such a clay may be very friable, it may not be re-

claimed and used again. An irreversible chemical change has taken place. This change, known as dehydration, is not accompanied by any shrinkage. If one were to open a kiln after it had been fired to about 500°, it would be noted that the ware was even more fragile than when it was put in the kiln and that no shrinkage had taken place.

### 3. Oxidation

Another important change which occurs in the clay during the early stages of firing is the oxidation or decomposition of all those components of the clay which are not already in oxide form. These would include such organic matter as carbon and the inorganic carbonates or sulphates. The oxidation of all these compounds is usually not complete until the temperature has advanced to about 900°.

All clays contain an appreciable amount of carbon, and firing has the effect of oxidizing or burning up this carbon. This process of oxidation requires that oxygen in the form of air be present in sufficient quantities in the kiln. Ordinarily oxidation proceeds without difficulty. However, if the firing is carried on too rapidly, or if insufficient air is present in the kiln because of improper adjustment of burners, some carbon may remain in the ware. This may cause blackening or, in the case of heavy clay products, blackening and bloating. Sometimes, when ware is tightly stacked together in the kiln, oxidation may be incomplete and a blackening or discoloration will be noticed. This is due to carbon still remaining in the fired piece.

Clay may contain small percentages of calcium carbonate or other impurities such as sulphates. As the firing advances, the dissociation point of these com-

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## CLAY

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### *Drying and Firing Clay*

pounds is reached and the carbon or sulphur is driven off. These impurities are ordinarily present in such small quantities that no problem attends their oxidation.

#### 4. Quartz Inversions

All clays contain an appreciable amount of quartz. This quartz may be associated with the clay in nature as an accessory mineral, or it may be quartz which has been added to the clay as flint. Crystalline quartz has a number of different forms, depending upon the temperature. When the temperature advances, the crystals of quartz rearrange themselves into a slightly different order, and these rearrangements are accompanied by slight changes in volume. Thus, when  $573^{\circ}$  is reached, quartz crystals undergo a change known as the change from alpha to beta quartz. This adjustment is marked by a slight ( $\pm 2\%$ ) increase in volume, which is reversible; that is, upon cooling the quartz changes from beta to alpha quartz and resumes its original crystalline form and size. This change of volume in the quartz portion of a clay body, although rather slight, must be accomplished slowly to avoid damage to the ware. If one part of an object in the kiln is heated up faster than another, the unequal expansion in the piece may cause it to crack. Care must likewise be taken in cooling so that the contraction which occurs at  $573^{\circ}$  may be passed safely. A large percentage of ware which comes from the kiln cracked is damaged by either too rapid heating or too rapid cooling at this critical temperature. Large objects particularly must be carefully fired at this temperature, especially if the kiln does not fire very evenly. Cracking which occurs during cooling is called dunting.

#### 5. Vitrification

As the temperature of firing increases beyond red heat, other changes occur in the clay which are called vitrification. Vitrification is the hardening, tightening, and finally the partial glassification of clay. Vitrification gives to fired clay its characteristic hard, durable, dense, and rocklike properties. It is accompanied by shrinkage in the clay. Vitrification proceeds gradually, at first causing the clay to be rather loosely compacted and then, with the advance of temperature, causing it to become increasingly hard, up to the point of melting and deformation. The same clay may be either very soft and chalklike or very dense, hard, and impervious, depending upon the temperature at which it is fired.

In part, this hardening results from fusions or melting of some of the components of the clay, more particularly those minerals, such as iron oxide, which are considered impurities. All substances melt at some degree of temperature, and clay, being usually a rather complex aggregate of numerous oxides, tends to fuse gradually. As the heat of the kiln advances, the more fusible impurities of the clay may melt into small beads of glass. These liquid beads of melted material soak into the surrounding area, binding the particles together like a glue, and act like a solvent in promoting further fusion. If the firing is carried on to a sufficient degree of heat, clay fuses completely into a liquid, which, upon cooling, is a glass. In practice, of course, we stop far short of this, but in the case of porcelain manufacture, such a complete fusion is approached, and the similarity between porcelain and glass is apparent. Some common red clays which contain a high percentage of iron and other impurities have a relatively low melting point. The tendency of these

clays to melt at temperatures of cone 8 to 11 has been utilized in making slip glazes, or glazes which are made up largely of fusible clay.

The strength of fired clay is due not only to glassification but also to the formation of new crystalline growths within the clay body, particularly the growth of mullite crystals. Mullite, which is an aluminum silicate, is characterized by a long needlelike crystal. These mullite crystals tend to grow at higher temperatures and extend themselves into the glassy matrixes within the clay. Mullite laces the structure together, giving it cohesion and strength.

Clays vitrify at various temperatures, depending upon their composition. A common red clay, for example, which is high in iron and other mineral impurities, may fire to hardness and density at about 1000° and may melt to a liquid at about 1250°. A pure kaolin body, on the other hand, may still be quite open and porous after having been fired to 1250° and may not melt until temperatures in excess of 1800° have been reached.

Further shrinkage occurs during vitrification. This shrinkage is due to the diminished size of the particles as they approach fusion and to the closer arrangement of particles in their glassy matrix. The firing shrinkage of a clay

is usually about the same as the drying shrinkage. Total shrinkage of a fired piece of clay may be as high as 10 percent, and this shrinkage will vary according to the degree of vitrification. However, when a clay actually begins to melt, it usually goes through a boiling or bloating stage and, at that point, may swell or grow in size, much as a cake rises from the distension of entrapped bubbles of gas.

The art of firing clay consists of bringing about just enough fusion and hardness in the material to serve the purposes at hand, but not of overfiring to the point of melting or the deformation of the shape of the ware. The desired extent of heat treatment, involving both time and temperature, is called maturing.

The well-fired piece of clay, then, is characterized by hardness, great compressive strength, denseness and impermeability to liquids, resistance to abrasion, chemical inertness and insolubility, and a very large and easily controlled variety of color and texture which is reminiscent of the variety in the earthy materials of the landscape. The one fault of clay wares, brittleness, may be, from the potter's point of view, an advantage, since the fragile nature of his product has ensured a steady demand for it.

## 1. Kaol

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## **RELATED PROCEEDINGS APPENDIX**

There are no decisions rendered by a Court or the Board regarding any related appeals or interferences.